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## EFFECTS OF WET AND DRY CYCLES ON TNT LOSSES FROM SOILS

by

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passed through XAD resin to trap volatile organic compounds followed by four sodium hydroxide traps in series to collect radiolabeled carbon dioxide. Carbon dioxide traps were analyzed after each cycle. At the end of the test, XAD traps were extracted and analyzed by liquid scintillation counting. Soils were extracted and analyzed by high performance liquid chromatography (HPLC) with both ultraviolet and radiation detectors. Soils were also combusted in a sample oxidizer, and the radiolabeled carbon dioxide was trapped and counted by liquid scintillation.

Radiolabeled carbon dioxide accounted for less than 1 percent of the tracer initially added to each test. Recovery of volatile organic carbon was 1 percent or less in all treatments. Therefore, volatile losses were minimal. Biotic treatments lost significantly more radiolabel than abiotic treatments. Results of HPLC analysis revealed more 4-amino-2,6-dinitrotoluene, a transformation product of TNT, than TNT in the soils. Complete combustion of the soils resulted in recovery of virtually all of the radiolabel. However, significantly greater recoveries from combustion data than from HPLC data revealed an average of 70 percent unextracted radiolabeled material in the soil. An unextractable residual in soils after prolonged contact with TNT has been reported previously. The existence of a residual is a potential source of error in current evaluations of TNT concentrations at contaminated sites and may result in significant underestimation of contamination hazard. The long-term stability of the residual and its ultimate contribution to environmental hazard is unknown.

Volatile losses of TNT or its decomposition products from soils were limited. Light exerted no effect on the limited losses observed. An average of 70 percent of the initial TNT treatment was unextractable by the standard method for analyzing TNT in soils. This large unextractable residual has important implications for assessing environmental contamination with TNT.

## PREFACE

This report was prepared by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The research was funded by the Discretionary Research Program, which is managed by Ms. Mary K. Vincent, Chief, Office of Technical Programs and Plans, WES. Personnel who cooperated in the execution of the study and the preparation of this report include Dr. Judith C. Pennington, Principal Investigator, and Ms. Cynthia B. Price of the Aquatic Processes and Effects Group (APEG), EL, and Ms. Charolett A. Hayes of AScI Corporation. Chemical analysis of soil samples was provided by Mses. Erica McCormick and Karen Myers of the Analytical Laboratory Group, EL, under the supervision of Ms. Ann B. Strong.

The report was prepared under the general supervision of Dr. Richard E. Price, Chief, APEG; Mr. Donald L. Robey, Chief, Ecosystem Research and Simulation Division; and Dr. John Harrison, Director, EL.

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CONVERSION FACTORS, NON-SI TO SI  
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
bars	100,000.0	pascals
cubic feet	0.02831685	cubic meters
inches	2.54	centimeters
torr (mmHg, 0 °C)	133.322	pascals

# EFFECTS OF WET AND DRY CYCLES ON TNT LOSSES FROM SOILS

## PART I: INTRODUCTION

### Background

Concentrations of 2,4,6-trinitrotoluene (TNT) in contaminated soils at munitions installations often greatly exceed the expected carrying capacity of soil water based on the aqueous solubility of the compound. This suggests the presence of a crystalline reservoir from which the soil solution is kept saturated through slow solubilization of TNT.

TNT is not remarkably volatile from the crystalline solid (vapor pressure at 20 °C is  $1.28 \times 10^{-6}$  torr) (Leggett, Jenkins, and Murrmann 1977). However, soil is a dynamic medium in which water content, microbial activity, and exposure to light are constantly changing. As soils are alternately wetted and dried, TNT from a crystalline reservoir may become a part of the soil solution, where degradation and volatilization are more likely to occur. Therefore, losses may occur through volatilization of the parent compound or of its microbial or photochemical transformation products, e.g., dinitrotoluene and trinitrobenzene, or through mineralization of the parent compound to yield carbon dioxide. If such mechanisms account for the significant TNT losses observed in the laboratory (Pennington 1988), remediation of TNT-contaminated soils may be promoted through exposing soils to controlled wet and dry cycles, coupled with tillage techniques to expose fresh soil surfaces to the atmosphere.

### Objectives

Objectives of the study were as follows:

- a. To quantify volatility of TNT and/or its degradation products from soils through wet and dry cycles.
- b. To determine the effects of light on volatilization of TNT and its degradation products from surface soils.

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\* A table of factors for converting non-SI units of measurement to SI units is presented on page 3.

## PART II: MATERIALS AND METHODS

### Test Chambers

A modification of a test chamber designed by Dr. W. F. Spencer, University of California, Riverside (Spencer et al. 1979), was adopted for this study. The chamber was constructed of two 1-in. cast aluminum blocks 30 cm long by 9 cm wide (Figure 1). The lower block contained a well 10 cm long by 3 cm wide. The upper block contained a 10-cm-long by 3-cm-wide hole lined on the bottom with a quartz glass sheet, 3.18 mm thick, for admission of light. The upper block was grooved to allow laminar flow of air across the surface of soil placed into the well of the lower chamber. The blocks were anodized with an electric current in sulfuric acid to seal the metal from the corrosive action of the soils.

### Test Soils

Two soils were used in the study, Sharkey clay and Tunica silt (Table 1). Particle size distribution was determined by the method of Day (1956) as modified by Patrick (1958). Total organic carbon was determined by American Public Health Association (1989) Method 5310 D. Cation exchange capacity (CEC) was determined by the ammonium saturation method (Plumb 1981). Extracts were analyzed according to EPA Standard Method 350.1 (U.S. Environmental Protection Agency 1982). Soil pH was determined on magnetically stirred soil slurries (1:2, soil:water) using a Beckman Model SS-3 pH meter (Beckman Instruments, Inc., Fullerton, CA). Oxalate extractable Fe, Al, Mn, and Ca were determined according to the method of Brannon and Patrick (1985). Metals were assayed on a Beckman Spectra Span IIIB Argon Plasma Emission Spectrophotometer (Applied Research Laboratories, Dearborn, MI).

Soils were amended with 80  $\mu\text{g}$  TNT/g dry weight of soil. One-tenth of the amendment consisted of [U-ring- $^{14}\text{C}$ ]TNT,\* or  $1.5 \times 10^6$  disintegrations per minute/g dry weight. Soils were amended by coating the walls of 125-ml jars with a methanol solution of radiolabeled plus unlabeled TNT and allowing the

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\* Specific activity of 20 mCi/mmol; radiological purity >98 percent by high performance liquid chromatography (HPLC) with radiation (radio) detector; chemical purity >98 percent by HPLC with an ultraviolet (UV) detector.

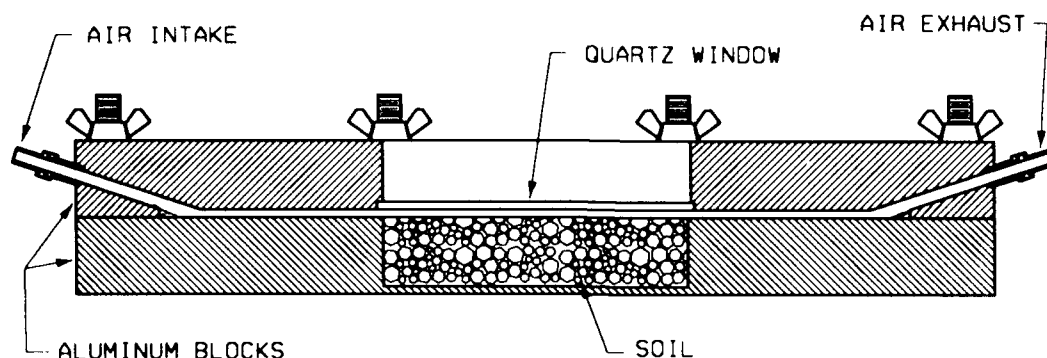


Figure 1. Test chamber

solvent to evaporate as the jar was slowly swirled under a radiological safety hood. Previous test results indicated that loss of TNT was insignificant during solvent evaporation. Soil (52 g and 37 g of clay and silt, respectively, on an oven-dried weight basis) and sufficient water to produce a 1:1 soil:water ratio were added to each jar. Jars were placed on a reciprocating box shaker for 24 hr at highest speed (280 excursions/min) to allow partitioning of contaminant from the walls of the container into the aqueous and solids phases. Results of kinetic studies conducted previously indicated that 24 hr was sufficient for steady state to develop. Amended soil slurry from a single jar was transferred to a single test chambers. Chambers for clay treatments contained an average of 46.8 g; chambers for silt treatments contained an average of 36.8 g.

#### Incubation

Once loaded with soil, the upper and lower blocks were sealed together with an o-ring and clamped with eight wing nut bolts. Predried air from a compressor was forced across the soil surface at 1 cu ft/min. Air exiting the chamber was passed through a 12-g Amberlite XAD-4 resin (Mallinckrodt, Inc., Paris, KY) trap for volatile organic compounds and subsequently through four 1N NaOH traps to collect  $^{14}\text{CO}_2$ . Air exiting the last trap was vented through a radiation safety hood.

The test was conducted in two replicates of each of the following conditions: (a) abiotic silt in light, (b) abiotic silt in dark, (c) abiotic clay in light, (d) abiotic clay in dark, (e) biotic silt in light, (f) biotic silt in dark, (g) biotic clay in light, and (h) biotic clay in dark. Abiotic

Table 1

Characteristics of Test Soils

Soil	Classification	pH	fOC*	Particle Size, %			CEC cmol <sub>c</sub> kg <sup>-1</sup>	Oxalate Extractable Metals, mg kg <sup>-1</sup>			
				Sand	Silt	Clay		Fe	Al	Mn	Ca
Sharkey clay	Very fine, montmorillonitic nonacid, thermic, Vertic Haplaquept	5.8	0.024	13.8	37.5	48.8	124.9	1,252	160	59.6	0.954
Tunica silt	Clayey over loamy, montmorillonitic, nonacid, thermic, Vertic Haplaquept	5.6	0.0057	0.0	93.8	6.25	17.2	252	196	152	1.10

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\* Fraction of organic carbon.

conditions were produced by exposing soils to a cobalt-60 gamma-ray source\* for 16 hr. This exposure time ensured at least one megarad of radiation to all parts of the sample. Tests exposed to light received approximately 254 nm of 490  $\mu\text{W cm}^{-2}$  at 16.5 cm through 1/8-in. quartz glass permitting 80 percent transmission of 310-nm wavelength or less. Tests were exposed for 8 of every 24 hr.

Treatments were taken through 13 wet/dry cycles. Soils were allowed to dry from field capacity (measured at 0.33 bar) to air-dried weight at ambient relative humidity ( $75 \pm 5$  percent) and temperature ( $25 \pm 2$  °C) before rewetting to field capacity by weight. Rewetting was accomplished by removing the upper plate and adding water until weight at field capacity was obtained. After completion of all cycles, soil samples were combusted in a Sample Oxidizer,\*\* and the radiolabeled  $^{14}\text{CO}_2$  was trapped in 20 ml of CarboSorb and Permafluor (1:1 v/v)\*\* and counted in a Packard TriCarb 2500 Liquid Scintillation Analyzer.\*\* Organic traps (XAD) were extracted three times with 10-ml portions of acetone and 1 ml of the extracts counted. NaOH traps were changed, and 1 ml was counted at the end of each cycle.

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\* The source, located at the Nuclear Sciences Department, Louisiana State University, consisted of an annular array of Co-60 rods and plates clad in stainless steel centered in a pit under 5.5 m of water. The total activity of the source was 3,071 Ci on 30 July 1986.

\*\* Packard Instruments Company, Inc., Meriden, CT.

### PART III: RESULTS AND DISCUSSION

#### Volatile Losses of $^{14}\text{C}$

Biotic treatments produced significantly more  $^{14}\text{CO}_2$  than abiotic treatments (Table 2). However, radiolabel recovered as  $^{14}\text{CO}_2$  accounted for less than 1 percent of the tracer initially added to each test. This result is an indication that TNT was not substantially mineralized during the test. However, the limited mineralization was primarily microbially mediated. These results were expected from soils with no prior TNT contamination because extended exposure times are required for degrading populations of microorganisms to become established. Neither soil type nor light/dark conditions affected  $^{14}\text{CO}_2$  evolution.

Radiolabel recovered from XAD traps was also low. Only the abiotic silt in light exhibited more than 1 percent of the tracer initially added. The percent recovery from this treatment was significantly greater than recoveries in XAD from any other treatments. This result suggests a light-mediated transformation of TNT to some volatile product. Since quantities were limited, other XAD extracts were not characterized by HPLC.

#### Analysis of Soils

##### Combustion analysis

As expected from the limited recoveries of radiolabel from  $\text{CO}_2$  and volatile organic (XAD) traps, results of soil combustion analyses indicated limited losses of radiolabel from the soil at the end of 13 wet/dry cycles (Table 2). Clay consistently lost more than silt, and biotic treatments consistently lost more than abiotic treatments, although differences were not always significant. Light conditions exerted no effect upon losses. The fact that clay has a significantly greater water-holding capacity (i.e., clay required a longer period of time to dry (an average of 7 days) than the silt (an average of 3 days)) may have resulted in greater microbial activity in the clay, which could account for the greater losses observed. Although biotic treatments exhibited greater losses than abiotic treatments, limited evolution of radiolabeled volatile organic compounds and  $\text{CO}_2$  indicated that transformation rather than mineralization predominated in the soil. Results of HPLC-UV analysis of soils confirmed transformation.

Table 2  
Percent Recoveries of Radiolabel from All Compartments

Treatment	Soil			VOCs XAD	CO <sub>2</sub> NaOH	Total*
	Combustion	Extraction/HPLC Radio	UV			
Clay light biotic	88.95	33.10	33.2	0.1688	0.4228	89.54
Clay dark biotic	92.92	31.02	32.8	0.1704	0.3522	93.44
Silt light biotic	99.66	23.94	21.2	0.4582	0.2630	100.38
Silt dark biotic	105.43	23.90	22.2	0.4199	0.2888	106.14
Clay light abiotic	98.19	37.52	31.2	0.0621	0.0946	98.35
Clay dark abiotic	98.47	34.96	33.4	0.0618	0.0936	98.63
Silt light abiotic	112.03	40.11	28.6	1.1991	0.1268	113.36
Silt dark abiotic	112.42	21.09	18.6	0.4925	0.1601	113.07

\* Sum of combustion, volatile organic compounds, and CO<sub>2</sub> recoveries.

#### Unextractable residual radiolabel

A comparison of recoveries of radiolabel from soils by combustion and by extraction for HPLC analysis showed significantly greater recoveries by combustion (Table 2). Differences between recoveries by combustion and HPLC-radio analysis revealed an average of 70 percent unextractable radiolabeled material in the soil. Therefore, extraction procedures were much less efficient than indicated by laboratory spikes produced by short-term exposure of TNT to soils. The unextractable residual pool of radiolabeled material derived from the parent TNT cannot be characterized by existing analytical techniques used for TNT analysis in soils.

An unextractable residual in soils after prolonged contact with TNT has been reported previously (Cataldo et al. 1989, Kaplan and Kaplan 1982, and Pennington 1988). After 61 days of incubation, Cataldo et al. (1989) found 31 to 54 percent of radiolabel remaining in [<sup>14</sup>C]TNT-amended soil after methanol extraction. Kaplan and Kaplan (1982) fractionated composted [<sup>14</sup>C]TNT-amended soils and found over 20 percent of the radiolabel remaining in the organic matter fractions after extensive solvent extraction. The compost was incubated for a maximum of 91 days. Pennington (1988) found an average of 35 percent unextracted radiolabel in soils from a [<sup>14</sup>C]TNT plant uptake study 65 days after amending. Both Kaplan and Kaplan and Cataldo et al. demonstrated that significant quantities of the unextracted residual is associated with the humic/fulvic fraction of the soil. Kaplan and Kaplan postulated that TNT or its transformation products become conjugated to humic materials

that are insoluble. Magalhaes, Shea, and Nelson (in review) confirmed that in [ $^{14}\text{C}$ ]TNT-amended soil subjected to composting, the humic plus fulvic acid fraction contained 36 to 44 percent of the bound residues. Less than 20 percent of the total  $^{14}\text{C}$  activity was acetone extractable.

The unextracted residual has potentially important implications for evaluating the extent and hazard of TNT contamination in the field. Current analytical methods may significantly underestimate actual contaminant levels. Furthermore, if the conjugates eventually decompose, they may release TNT or hazardous decomposition products of TNT into the environment where they are potentially available to groundwater and biota. If conjugates have extremely long half-lives, development of techniques to promote their formation in situ should be pursued.

#### Degradation products

Results of HPLC analysis of soils indicated significantly greater quantities of 4-amino-2,6-dinitrotoluene (4A) than TNT in all treatments (Tables 3-4). The common detection of 4A in field soils contaminated with TNT for years and in laboratory soils amended with TNT suggests that amination of the para-nitro moiety on the TNT molecule is an easy reaction. Clay treatments produced more 4A than other treatments, although differences were not always significant (Table 5). The extended period of time the clay treatments were wet may support both biotic and abiotic transformation of TNT to 4A. Biotic treatments were generally greater in 4A than abiotic treatments, but differences were not often significant. Microbial transformation to 4A is known to occur in soils (Kaplan and Kaplan 1982). The high 4A concentrations may be attributed to a slow buildup of microbial activity in treatments during the incubation period. Test chambers were opened 13 times; therefore, the chances for introducing microorganisms were great. Even if test chambers remained strictly abiotic throughout the test, residual microbial enzyme activity attenuated by the soil after irradiation may account for 4A production in abiotic tests. Chemical, as opposed to microbial, transformation cannot be ruled out even though abiotic transformation of TNT into 4A in soils has not been confirmed.

The only other decomposition products detected, TNB and 2,4DNT, were below the acceptable detection limit (Table 3). Recoveries using HPLC-UV and HPLC-radio detectors were similar.

Table 3  
Results of HPLC-UV Analysis of Soils, mg/kg

Treatment	TNT	TNT Transformation Products*					
		TNB	DNB	2,4DNT	2,6DNT	4A	2A
Clay light biotic	3.88	0.135 <sup>J</sup>	<0.250	<0.250	<0.250	29.18	<0.250
Clay dark biotic	3.91	<0.250	<0.250	0.194 <sup>J</sup>	<0.250	28.71	<0.250
Silt light biotic	2.40	0.132 <sup>J</sup>	<0.250	<0.250	<0.250	18.62	<0.250
Silt dark biotic	1.28	0.150 <sup>J</sup>	<0.250	<0.250	<0.250	20.72	<0.250
Clay light abiotic	11.55	0.136 <sup>J</sup>	<0.250	<0.250	<0.250	19.46	<0.250
Clay dark abiotic	11.26	0.188 <sup>J</sup>	<0.250	<0.250	<0.250	21.91	<0.250
Silt light abiotic	13.88	0.200 <sup>J</sup>	<0.250	<0.250	<0.250	14.47	<0.250
Silt dark abiotic	2.22	<0.250	<0.250	<0.250	<0.250	16.37	<0.250

\* Transformation products of TNT included 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (2,4DNT), 2,6-dinitrotoluene (2,6DNT), 4-amino-2,6-dinitrotoluene (4A), and 2-amino-4,6-dinitrotoluene.

<sup>J</sup> Values designated with J were detected below statistically acceptable detection limits of 0.250 mg/kg.

Table 4  
Percent Recoveries of Radiolabel in Soils by  
HPLC-Radio Analysis\* (Standard Error)

Treatment	TNT	4A
Clay light biotic	5.86 (0.74)	27.24 (2.64)
Clay dark biotic	4.36 (0.91)	26.66 (1.52)
Silt light biotic	3.62 (0.62)	20.32 (2.98)
Silt dark biotic	2.44 (0.064)	21.46 (1.95)
Clay light abiotic	14.52 (0.26)	23.00 (2.17)
Clay dark abiotic	9.20 (1.34)	25.76 (2.17)
Silt light abiotic	20.74 (3.01)	19.37 (2.91)
Silt dark abiotic	1.89 (1.89)	19.60 (0.34)

\* HPLC-UV was used to identify the two peak as TNT and 4A.

Table 5  
Duncan Grouping of Mean Concentrations of  
4A in Soils by HPLC-UV, mg/kg

<u>Treatment</u>	<u>Mean</u>	<u>Duncan Grouping*</u>	
Clay light biotic	29.18	A	
Clay dark biotic	28.73	A	
Clay dark abiotic	21.95	A	B
Silt dark biotic	20.72		B
Clay light abiotic	19.46		B
Silt light biotic	18.62		B
Silt light abiotic	14.74	B	C
Silt dark abiotic	10.41		C

\* Means followed by the same letter are not significantly different. The test was conducted at the 0.05 level of significance.

#### PART IV: CONCLUSIONS

Volatile losses of TNT or its decomposition products from soils were limited. Biotic treatments produced significantly more  $^{14}\text{CO}_2$  than abiotic treatment, indicating that some microbial mineralization occurred. Volatile organic recoveries were also low. The highest value was found in an abiotic light treatment, suggesting that the transformation to volatile products was not microbial, but light mediated. Treatments receiving light did not differ from dark treatments.

The discovery of 70 percent unextractable radiolabeled material in the soil indicates that the currently used extraction procedure is inefficient for assessing environmental contamination by TNT residuals, or conjugated TNT decomposition products. The characterization and long-term stability of the residual have potentially important implications for evaluating the extent and hazard of TNT contamination in the field.

In soils analyzed by HPLC, significantly more 4A than TNT was found. This result suggests that amination of the para moiety on the TNT ring occurs readily in the soil through wetting and drying cycles. Higher concentrations of 4A than TNT appeared in all treatments, indicating that the transformation may be mediated by chemical as well as microbial processes.

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